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ro:	Carol Peterson Registration D					
FROM:	Elizabeth Behl Acting Section Ground Water To Environmental	Head		By a y ch / EF	To for CB	
THRU:	Henry Jacoby, Environmental	Chief (H750 Fate & Ground	7C) d Water	HMY CO	ED PLOOP	
Attached, please find the EFGWB review of:						
Reg./File	#:		······································			
Chemical Name: <u>Tebuthiuron</u>						
Type Prod	uct: <u>Herbicide</u>	- nonagricu	ltural u	se and ran	nge land	
Company N	ame: <u>Dow Elan</u>	co	· · · · · · · · · · · · · · · · · · ·	and the state of t	· · · · · · · · · · · · · · · · · · ·	
Purpose: Tebuthiuron - Small-Scale Retrospective Study - Protocol Study Site: Kenedy Ranch Sarita, Texas.						
Date Rece	ived: <u>05/25/90</u>		ACTION	CODE: _	665	
Date Comp	lete: <u>10/4/91</u>		EFGWB #	(s): <u>9</u> (0-0596	
Monitoring Study Requested: x Total Review Time: 4.5 Days						
Monitorin	g Study Volunta	ry:				
Deferrals	To:	Biological	Effects	Branch		
		Science Int	egration	& Policy	Staff, EFED	
	and the second s	Non-Dietary	Exposur	e Branch,	HED	
	district the state of the state	Dietary Exp	osure Br	anch, HED		
		Toxicology	Branch,	HED		

REVIEW OF SMALL-SCALE RETROSPECTIVE GROUND WATER MONITORING STUDY - Kenedy Ranch - Sarita Texas

1. CHEMICAL:

Chemical name: N-[5-(1,1-Dimethyl ethyl)-1,3,4-thiadiazol-2-

yl]-N,N'-dimethylurea

Common name: TEBUTHIURON

Trade name: Herbic, Graslan, Perflan, Spike

Structure: Not Applicable

Physical/Chemical Properties:

Chemical Formula $C_9H_{16}N_4OS$ Molecular Weight 228.31 Water Solubility 2,500 mg/L @20 c 0.02 to 2.03 2.0 x 10 torr Vapor Pressure

Log Octanol/Water

Partition Coefficient

1.79

Field dissipation

half-lives

365 to > 1350 days

Aerobic soil metabolism 273 days Anaerobic soil metabolism >336 days

2. TEST MATERIAL: Not Applicable.

3. STUDY/ACTION TYPE:

Review protocol for small-scale retrospective ground-water monitoring study for tebuthiuron.

4. STUDY IDENTIFICATION:

Title: Tebuthiuron - Small-Scale Retrospective Ground-Water Study - Protocol Study Site: Kenedy Ranch Sarita Texas

Author:

C. T. Stone and J. R. Bowes The Johnson Company, Inc.

Environmental Sciences and Engineering

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Submitted by:

Dow Elanco

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Identifying No: 0054

Case:

Submission:

Record Number: 264871 DP Barcode:

Action Code: 665

Date Sent to EFED: 05/16/90 Date Received by EFED: 05/25/90

5. Reviewed by: James K. Wolf Soil Scientist

OPP/EFED/EFGWB/GWTS

Signature: <u>James K. Woff</u>

Date: <u>1/19/91</u>

6. Approved by: Elizabeth Behl Acting Section Head OPP/EFED/EFGWB/GWTS

Signature: I-CANT

7. **CONCLUSIONS:**

The intended purpose of the document reviewed appears to be three fold. The first was to provide site characterization data to justify and demonstrate the suitability of the site for the a small-scale retrospective ground-water study. The second was to define the protocol to be followed, during the remainder of this study. The third intent of the document was to present some preliminary data on levels of tebuthiuron in soils and ground water, collected during the site characterization phase.

These objectives appear to have been met. The proposed study site is acceptable and most likely represents a real worst-case condition.

Overall, the protocol is relatively complete and well thought out, although there are several areas lacking in specific detail. The SOP's provided by the Johnson Company, Inc. are generally adequate to define the scope of work, but in most instances additional study-specific information will be required for each study protocol. The document acknowledges the need for specific detail, which will depend upon the objectives of the study (Introduction to SOP-JCO-003, Appendix 3, page 1 of 16). Therefore, more specific detail should be added to the generic SOP's. A number of topics have been identified that should be incorporated into future studies, if it is too late for inclusion in this study. Some of this additional information or detail has been included in the Small-Scale Retrospective - Study Protocol report, but deficiencies still remain.

The results of the preliminary data from this small-scale retrospective study indicate that tebuthiuron residues have leached from surface soils to the lower soil profile (in the vadose zone) when restricting layers are present, and to ground water when restricting layers are not present. The

preliminary data show that tebuthiuron is persistent as residues remain in the vadose zone and ground water four years after application.

8. RECOMMENDATIONS:

A. The locations of the four "RSE" samples (page 11 and 12, and Table 3) could not be determined. The locations should be delineated on Figure 3 or a map similar to Figure 3. The locations of all monitor wells, observation wells, soil sample sites, etc. should be clearly identified and shown (see Discussion Section of this document).

B. 7.6.3.1 Sample Transport, page 19

The report portion of the protocol document (Sections 1 to 10) indicates that because the ground-water temperatures are warm (18-20 °C) maintaining sample temperatures at 4°C may be difficult during transport. Low temperatures and other preservation techniques are normally used during sample transportation and storage because of a concern for sample preservation (i.e., retard biological action and chemical reactions). Therefore, the registrant should investigate the stability of the tebuthiuron and metabolites during transport of the sample from the field to the laboratory.

C. 7.6.3.3 Analytical, page 20

The registrant indicates that a new method will be used to measure tebuthiuron and its metabolite levels in water. The registrant should, therefore, demonstrate and quantify the methods of detection, detection limits and recoveries for known samples.

- D. Some suggestions concerning the presentation of information are also given in the Discussion section of this document.
- E. The protocol document should be edited to ensure that all references and cross-references to information are correct.

9. BACKGROUND:

Tebuthiuron is a herbicide used for total vegetation woody plant control in noncrop areas and for brush and weed control in rangeland areas. Tebuthiuron moves into the soil root zone where it is absorbed by the roots of woody plants. For susceptible woody plants, tebuthiuron inhibits photosynthesis, resulting in death normally in one to three years after application (after Johnson report, citation Elanco Products Company, 1983). The Johnson company (after

Elanco Products Company, 1983) indicates that for selective woody plant control it may not be necessary for reapplication for periods up to 20 years.

Environmental Fate: The herbicide tebuthiuron is resistant to hydrolysis and photolysis. Aerobic metabolism for a loam soil indicated a half-life of more than 273 days and anaerobic soil metabolism for a loam soil was greater than 336 days with compound 104 being the major degradate. Field dissipation half-lives are quite long ranging from 365 to 450 days in areas with moderate to heavy rainfall and up to 1350 days in low rainfall areas. The compound is very mobile in loam, loamy and sandy soils and less mobile in silty loam soils. Soil partition coefficients (Kd) values range from 0.11 to 1.82 mL/g. Selected environmental chemistry and fate characteristics for tebuthiuron compared with those of some pesticides that have been found to leach are listed in Table 1.

A small-scale retrospective ground-water monitoring study was required by a Data-Call-In notification (May 24, 1988). The registrant DowElanco is presently conducting a small-scale retrospective ground-water monitoring study for Tebuthiuron. The study is being conducted at the Kenedy Ranch, located near Sarita in southern Texas. Tebuthiuron (Spike 20P) was aerially broadcast by helicopter on March 24, 1986.

10. <u>DISCUSSION</u>:

The study is being conducted at the Kenedy Ranch which is located near Sarita in southern Texas. Tebuthiuron was applied in 140 foot wide strips (a 70' swath with two swaths/strip) to a portion of an area of approximately 720 acres, on March 24, 1986 at the rate of 1 to 2 lb-a.i./acre in a fenceline application area and 3.5 to 4 lb-a.i./acre in spray overlap areas.

Site geology consists of eolian sands overlying fluvial deposits. Soil analytical data show that the soils have low clay (4 to 8%) and organic matter (0.1 to 0.7%) content. Particle size distributions of the soil material in the vadose zone were not determined, but drilling logs indicated the textures are primarily very fine sands to sandy clay loams. The drilling logs also indicated that restricting layers, such as caliche and thin clay layers, are present at some locations.

Tebuthiuron Detections in Soil: Soil samples, collected (June and November, 1989) and analyzed during the site characterization phase, were taken in approximately 1 foot increments down to a depth of about 5 feet (4.0 to 5.5 feet)

at four sites ("RSE" sampling site locations not shown). Tebuthiuron residues were detected in some of these soil samples (Table 3, page 12 of the protocol document). The protocol document reports that tebuthiuron residues have leached and are accumulating above an impeding soil layer. Where no impeding layer is present, residues have leached beyond the depth of soil sampling (60 inches). The detections from the four "RSE" samples are summarized below:

Locatio	n Dep	th Tebu	thiuron	(conce	entration)
RSE	1: 0.0-	0.5' 7.0	ng/g (0.014	lbs/acre)
RSE	2: 0.5- 1.5- 2.0-	2.0' 16.0	ng/g (0.033	lbs/acre) lbs/acre) lbs/acre)
RSE	3: 0.0- 4.0-				lbs/acre) lbs/acre)
RSE	4: 2.7- 3.5-				lbs/acre) lbs/acre)

The protocol states that additional soil samples will be collected down to 120 inches, or the top of water, or refusal (condition when the downward moved of an auger or slip-spoon sampler is impeded), whichever is encounter first (page 19).

Tebuthiuron Detections in Ground Water: Tebuthiuron residues were also detected and confirmed in a down-gradient monitoring well (MW-104) from samples collected in November 1989 and February 1990. No detections have been observed in the other monitoring wells (MW-101, MW-102, MW-103, and MW-105) at the time that this report was submitted. The concentrations of tebuthiuron in MW-104 have ranged between 3.0 and 4.0 ng/L using an analytical procedure with a reported limit of quantification of about 1.0 ng/L.

Page 19 of the Protocol, indicates that an additional monitoring well will be installed about 30 feet to the southeast and downgradient from monitoring well MW-104. Additional soil samples (7.8 Methodology of Site Sampling: Soil Sampling, page 21) will be collected down to 120 inches or top of water table, or refusal, whichever is encountered first. Preliminary soil samples were collected down to approximately 60 inches (Table 3, page 12).

Specific Comments

During a brief telephone discussion with Mr. Christopher

Stone of the Johnson Company, Inc., on September 25, 1991, he indicated that the study was nearly completed. Therefore, this review will probably have more of a bearing on future or additional work. Overall, the protocol is acceptable. The following discussion refers to specific portions of the protocol or appendices.

- 1. The caption for Table 3, page 12, should provide some additional information so that it may better stand alone. All tables and information or data presented in the appendices should contain adequate information so that they can more or less stand alone. Information to add to the tables in the final report should include: sampling dates, location of samples, analytical method or procedure used, and a study citation.
- 2. <u>7.8 Methodology of Site Monitoring:</u> Soil Sampling, page 21 and Appendix 11, SOP-JCO-017 Soil Core Sampling: Pesticide Residues.

Several problems or deficiencies exist concerning the soil sampling protocol. The major areas of concern are compositing soil samples and the length of the soil sampling increments.

- a. Compositing of soil samples is generally not acceptable as no information concerning variability can be obtained. Limited compositing may be acceptable, but the compositing scheme should be fully specified in the protocol.
- b. The length of the soil increments is also too general. While it is agreed that sampling increments may need to vary depending on soil conditions (i.e., soil horizons, color changes, unique soil conditions, etc.) and the objectives of the study, some discussion is necessary to specify a maximum sampling increment.
- c. Part D. Sample shipping and handling (Appendix 11, SOP-JCO-017, Sheet 5 or 6). The SOP discusses the shipping and handling of soil cores whereas the discussion on page 21 discusses composited samples. This needs clarification.
- d. If samples are to be composited, who and how will the determination to composite samples be made? The compositing of soil samples should be based on a predetermined system that is defined in the protocol and on observations made in the field, not on the whims of an analyst in a laboratory.

3. <u>9.2.1 Data Preparation</u>, page 25

When duplicate samples are reported as averages, state that the value is an average and provide the raw data in an appendix. This is necessary to get an indication of sampling variability and laboratory precision.

4. 10.0 Final Report, page 28

The registrant indicates that semi-annual progress reports will be submitted to the EPA while the study is being conducted. It is not know if any progress reports have been submitted by the registrant since the submission of this document on May 16, 1990. A schedule of when progress reports are to be submitted should be specified.

5. Appendix 1.

- a. Page 1 indicates tebuthiuron use information is included in Appendix 1. This data could not be located and therefore should be provided. Appendix 1 was apparently used in another presentation because many references cited are not correct and some information referenced is not included in the document. For example, page 3 makes reference to a map in Appendix 2 showing the general locations of the sites evaluated. This map was not included. Page 4 references photographs in Appendix 2 that were not found. Page 5 indicates that photographs and a map for the Swickheimer Ranch are located in Appendix 4.
- b. Page 3 was missing from the document. A call was placed to Mr. Christopher Stone of the Johnson Company to obtain a copy of the missing page. The missing page was received on September 30, 1991.
- c. Page 3 makes reference to soil survey, maps and photos being in Appendix 3. Appendix 3 actually contains well construction and installation protocol not soil survey information. Some of the information alluded to on page 3 of Appendix 1 appears to be missing; Appendix 2 contains some of the above mentioned soil survey information.

6. Appendix 2.

a. A table of contents with page numbers for Appendix 2 would greatly facilitate the evaluation of the information presented in the appendix. The data presented in Appendix 2 should also include more descriptive information. For example, the permeameter test results should more fully explain which specific "permeameter" method was used so that the table can more fully stand alone. The SOP for this measurement should also be provided. The units "min/in" would seem to indicate a percolation test using a falling head rather than a constant head method.

- b. The methods used for all soil analysis should be specified and references given. If other than standard methods are used or methods are modified, the laboratory procedures should also be submitted.
- c. Soil description SEP-103, sheet 3 of 14 identifies OW104 (observation well) which could not be found on Figure 3.
 Is OW-104 the same as MW-104? The locations of OW-101 to
 OW-105 and OW-201 to OW-203 could not be located. Sampling
 locations for SEP 101, SEP 102, SEP 104, SEP 106, SEP 107
 could not be found. Please locate these on a map. Soil
 descriptions for the "Soil Descriptions" using the SEP
 prefix are not complete, as no soil horizon delineation are
 provided. Were the depth increments selected by soil
 horizon or arbitrarily divided?
- d. Drilling Logs: Do the four numbers (i.e., MW-101 0.0-2.0': 1,2,2,3) listed to the right of the depth increment indicate the "number of blows per 6 inches" for the split-spoon sampler? Please clarify.
- e. In the future soil colors should be determined and identified by Munsell color chart system. This allows for some consistency for soil colors and also corresponds to SCS profile characterization methodology and profile descriptions ("Blue Sheets" typifying pedon descriptions). Additionally, SCS typifying pedon and mapping unit descriptions should be included. Munsell colors for the drilling logs is also desirable.
- f. The table summarizing the split-spoon samples is a poor reproduction and is difficult to read, please submit a more legible reproduction.
- g. Soil borings should be continuous rather than sampling alternate two-foot long increments. The continuous sampling is important in the identification of restricting layers which can impede water flow. Particle-size distribution should also be determined for each sampling increment.
- h. It is not specified what are the units on the Ground Water Conductivity (note typo Conductivity) distribution figure. The units should be specified.
- i. It is recommended that weather conditions for field work be added to the data sheets.
- j. The protocol indicates that decontamination procedures are to be followed. Where will the drilling equipment be decontaminated? If on site, where will the

decontamination area be located? Where was (or will) the water be disposed when pumped from the wells during well development and purging?

TABLE 1. Related environmental chemistry and fate characteristics for tebuthiuron compared with those of some pesticides that have been found to leach.

Name of Characteristics	Known leacher ¹ Characteristics	Tebuthiuron Characteristics
Kd	< 5, usually less 1 or 2	than 0.11 to 1.82
Koc	< 300 to 500	4
Water solubility Kw (mg L ⁻¹)	> 30	2500
Vapor Pressure	$<1.5 \times 10^{-10}$	2.00 X 10 ⁻⁶
Henry's Law Constant (atm mol	< 10 ⁻⁵	2.40 X 10 ⁻¹⁰
Photolysis in wat t _{1/2} (days)	er, > 7	resistant
Photolysis in soi t _{1/2} (days)	1 > 14 to 21	39.7 sandy loam
Hydrolysis, t _{1/2} (days)	> 175	pH 3,6,9 > 64 days
field dissipation t _{1/2} (days)	ı	>365
leaching depth	36 inches	60+ inches at Texas study site

Cohen et al., 1984.
Trigger factors

REFERENCES

Cohen, S.Z., Creeger, S.M., Carsel, R.F., Enfield, C.G. 1984.

Potential for pesticide contamination of ground water resulting from agricultural uses. pp. 297-325. <u>IN</u> Treatment and Disposal of Wastes. (Eds.). Grueger, R.F., Seiber, J.N. ACS Symposium Series No. 259, American Chemical Society. Washington DC

Elanco Products Company. 1983. Graslan Technical Manual.